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The Crystal Structure of the 1:2 Phenanthroline Adduct of Sodium Oxotricyano-1,10-phenanthrolinemolybdate(IV)

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The crystal structure of $Na[MoO(CN)_3(Phen)]\cdot 2Phen$ *was determined from three-dimensional X-ray data. The green crystals are triclinic, space group* $P\bar{1}$, *with cell dimensions* a = *13.354,* b = *14.380,* c = *9.294* Å, α = *93.53,* β = *97.05,* γ = *104.93° and containing two molecules per unit cell. The structure was solved from 3353 observed reflections which were obtained from a computer automated diffractometer. The anisotropic refinement converged to* R = *0.069.*

The anion is a distorted octahedron. The Mo–N distance (2.363(7) Å*),* trans *to the Mo=O bond (1.659(7)* Å*), is significantly 0.189* Å *longer than the other Mo–N bond. The* mer-*arrangement of cyanide ligands has two normal* $Mo–C_{av}$ = *2.17(1)* Å *bond distances and a significant shorter Mo–C = 2.092(9)* Å *bond* trans *to the shorter Mo–N bond. The sodium ion has a distorted trigonal prismatic environment of six N atoms.*

Introduction

The structurally characterized oxocyanide complexes of molybdenum(IV) comprise the $MoO_2(CN)_4^{4-}$ [1], $MoO(OH)(CN)_4^{3-}$ and $MoO(H_2O)(CN)_4^{2-}$ ions [2]. Salts of the *trans*-dioxotetracyanomolybdate(IV) ion can only be isolated in strong alkaline medium. Successive facile protonations yield the oxo-hydroxo and oxo-aquo species in weakly alkaline solution. Structural data also indicate increasing double bond character for the Mo=O bond distances, ranging from 1.834(9) Å in the O=Mo=O to 1.698(7) Å in O=Mo–OH and 1.668(5) Å in the $O=Mo–OH_2$ moieties. This bond shortening must lead to increasingly *trans*-labilization of the Mo–OH (2.007(7) Å) but more so for the $Mo–OH_2$ (2.271(4) Å) bond.

Against this background, we performed preliminary investigations involving substitution reactions with mono- and bidentate ligands on the protonated species of the $MoO_2(CN)_4^{4-}$ ion. Both type of ligands, especially those containing N, O and S donor atoms, gave positive reaction but crystalline products could only be isolated for 1,10-phenanthroline (phen) and its methyl-substituted derivates. Element analyses and IR spectra coupled with relative high molecular weights were insufficient in assigning a correct formula since it is also known that μ-oxo dimeric anions, $[M_2O_3(CN)_8]^{n-}$, for Mo(IV) [3], W(IV) [4] and Re(V) [5] do exist. Substitution products from this origin was thus also a possibility. This structure determination gives positive identification to the product and also serves to indicate which ligand sites of the parent complex has undergone substitution. This would be helpful for a detailed mechanism based on kinetic studies.

Experimental

$K_4Mo(CN)_8\cdot 2H_2O$ was prepared as described previously [6]. $NaK_3[MoO_2(CN)_4]\cdot 6H_2O$ was prepared in a similar manner employed for the isomorphous tungsten complex [7] with the following alterations: Irradiation of $K_4Mo(CN)_8$ was performed in a 1 *M* NaOH solution in direct sunlight for *ca.* 1.5 hr without protection of an inert gas atmosphere. Slow precipitation (2–6 hr) with addition of a 50% (w/v) mixture of KOH–NaOH (3:1 molar ratio) gave large rose pink crystals which were less susceptible to atmospheric attack by CO_2. The crystals (70% yield) were stored under dry nitrogen over silica gel.

The phen complex was prepared as follows: To a solution of 0.48 g (0.001 mol) $NaK_3[MoO_2(CN)_4]\cdot 6H_2O$ in 30 cm^3 0.2 *M* $NaHCO_3$ was added 10 cm^3 of a 50% MeOH/EtOH solution containing 0.38 g (0.002 mol) 1,10-phenanthroline monohydrate. The dark green solution was tightly covered with a transparent film and set aside for *ca.* 3 days after which green crystals (40% yield) were obtained.

Crystal Data

$C_{39}H_{24}N_9ONaMo$, molecular weight 753.6, triclinic space group $P\bar{1}$, *a* = 13.354, *b* = 14.380, *c* =

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TABLE 1. Fractional Atomic Coordinates ($\times 10^4$) and Thermal Parameters ($\times 10^3$) with Estimated Standard Deviations in Parentheses.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	2476.5(6)	407.5(6)	1867.4(9)	36(1)	44(1)	37(1)	9(1)	7(1)	8(1)
C(1)	152(7)	−712(7)	1968(11)	37(5)	45(6)	53(6)	3(4)	−5(4)	9(5)
C(2)	−743(8)	−1195(7)	2570(11)	43(6)	45(6)	60(7)	4(5)	1(5)	11(5)
C(3)	−652(7)	−1046(7)	3991(12)	32(5)	43(6)	69(7)	5(4)	13(5)	3(5)
C(4)	515(8)	−1323(7)	6324(10)	58(6)	38(5)	44(6)	18(5)	21(5)	14(4)
C(5)	1504(8)	−1033(7)	7116(10)	59(6)	45(6)	42(6)	15(5)	15(5)	9(5)
C(6)	3419(8)	−226(7)	7224(10)	59(6)	47(6)	46(6)	30(5)	−4(5)	−8(5)
C(7)	4221(7)	272(7)	6496(11)	41(5)	47(6)	52(6)	21(5)	−1(5)	−8(5)
C(8)	3982(7)	457(7)	5037(10)	46(6)	40(5)	43(5)	17(4)	−6(4)	−1(4)
C(9)	2223(7)	−346(6)	4991(9)	36(5)	26(4)	41(5)	8(4)	6(4)	6(4)
C(10)	1221(7)	−643(6)	4165(9)	35(5)	36(5)	37(5)	9(4)	8(4)	5(4)
C(11)	359(7)	−1131(6)	4832(10)	36(5)	29(5)	55(6)	19(4)	10(4)	6(4)
C(12)	2389(7)	−541(6)	6462(10)	42(5)	40(5)	42(5)	20(4)	10(4)	1(4)
C(13)	7471(8)	5300(7)	1313(12)	52(6)	44(6)	72(7)	5(5)	16(5)	−3(5)
C(14)	7669(9)	6279(8)	1024(13)	54(7)	66(8)	64(7)	2(6)	21(6)	−1(6)
C(15)	7111(9)	6520(7)	−157(13)	61(7)	40(6)	75(8)	7(5)	29(6)	−1(5)
C(16)	5691(9)	5989(8)	−2277(11)	69(7)	50(6)	56(6)	22(6)	22(6)	16(5)
C(17)	4934(8)	5280(8)	−3102(11)	54(6)	65(7)	53(6)	25(6)	15(5)	16(5)
C(18)	3981(8)	3525(8)	−3562(12)	53(6)	56(7)	62(7)	13(5)	6(5)	−2(5)
C(19)	3810(8)	2599(8)	−3136(11)	55(6)	55(7)	54(6)	15(5)	10(5)	−16(5)
C(20)	4440(8)	2454(7)	−1853(11)	60(6)	53(6)	52(6)	18(5)	6(5)	−6(5)
C(21)	5344(7)	4062(6)	−1517(9)	40(5)	36(5)	42(5)	14(4)	17(4)	2(4)
C(22)	6164(7)	4825(6)	−661(10)	45(5)	29(5)	49(5)	15(4)	23(4)	5(4)
C(23)	6321(8)	5789(7)	−1038(11)	51(6)	46(6)	55(6)	18(5)	27(5)	8(5)
C(24)	4766(8)	4296(7)	−2728(10)	54(6)	48(6)	42(5)	24(5)	15(5)	7(5)
C(25)	6450(9)	2805(9)	4517(12)	74(8)	86(9)	55(7)	26(7)	33(6)	11(6)
C(26)	6777(13)	2800(11)	6013(14)	110(12)	108(11)	53(8)	26(9)	25(8)	19(7)
C(27)	7833(13)	3036(13)	6535(14)	102(12)	145(15)	52(8)	15(11)	17(8)	9(8)
C(28)	9681(12)	3573(10)	6031(16)	78(9)	83(10)	91(10)	15(8)	−22(8)	−10(8)
C(29)	10368(10)	3820(10)	5105(17)	61(8)	70(9)	106(11)	9(7)	−14(8)	1(8)
C(30)	10706(11)	3979(12)	2555(17)	67(9)	117(12)	122(13)	33(8)	37(8)	22(10)
C(31)	10317(13)	3922(15)	1131(19)	84(11)	192(19)	118(14)	50(12)	56(10)	34(13)
C(32)	9207(13)	3646(15)	712(17)	88(11)	200(20)	90(11)	42(12)	38(9)	30(12)
C(33)	8916(8)	3512(7)	3052(11)	44(6)	49(6)	64(6)	23(5)	16(5)	10(5)
C(34)	8181(8)	3295(7)	4072(10)	51(6)	41(5)	48(6)	10(5)	0(5)	1(4)
C(35)	8557(9)	3324(9)	5559(12)	70(7)	81(9)	51(7)	20(6)	−4(6)	−3(6)
C(36)	10002(9)	3764(7)	3579(14)	63(7)	39(6)	98(9)	26(5)	13(6)	8(6)
C(37)	2934(7)	−898(7)	1337(9)	40(5)	47(6)	36(5)	9(4)	11(4)	2(4)
C(38)	2342(7)	1725(7)	3025(9)	35(5)	42(5)	37(5)	12(4)	13(4)	10(4)
C(39)	4030(7)	1176(7)	1674(11)	38(6)	47(6)	56(6)	6(5)	14(5)	9(5)
N(1)	1108(5)	−422(5)	2756(8)	35(4)	34(4)	42(4)	12(3)	9(3)	4(3)
N(2)	3021(5)	154(5)	4297(7)	34(4)	39(4)	33(4)	9(3)	2(3)	−3(3)
N(3)	6748(6)	4586(5)	492(9)	51(5)	40(5)	52(5)	9(4)	12(4)	1(4)
N(4)	5194(6)	3159(5)	−1082(8)	53(5)	34(4)	36(4)	13(4)	14(4)	−0(3)
N(5)	7152(6)	3034(6)	3566(8)	51(5)	63(6)	44(5)	15(4)	8(4)	8(4)
N(6)	8522(8)	3434(8)	1633(10)	68(6)	107(8)	56(6)	32(6)	24(5)	15(5)
N(37)	3137(7)	−1579(6)	901(9)	71(6)	58(6)	54(5)	22(5)	20(5)	−2(4)
N(38)	2234(7)	2422(6)	3603(10)	50(5)	54(6)	66(6)	19(4)	16(4)	4(5)
N(39)	4878(7)	1614(6)	1540(10)	52(6)	60(6)	64(6)	11(5)	19(4)	15(5)
O	1786(6)	465(6)	273(7)	64(5)	79(5)	45(4)	22(4)	−0(3)	11(4)
Na	6469(3)	2789(3)	860(4)	49(2)	50(2)	41(2)	13(2)	7(2)	7(2)

9.294 Å, $\alpha = 93.53$, $\beta = 97.05$, $\gamma = 104.93°$, $Z = 2$, $\mu(\text{MoK}\alpha) = 4.47\ \text{cm}^{-1}$, measured density = 1.48 g cm^{-3}. Three-dimensional intensity data were collected for θ values between 3 and 23° on a Philips PW 1100 four circle single crystal X-ray diffractometer using graphite monochromated MoKα radiation (λ = 0.7107 Å). A crystal with dimensions of 0.05 × 0.23 × 0.23 mm^3 was used for the data collection. No

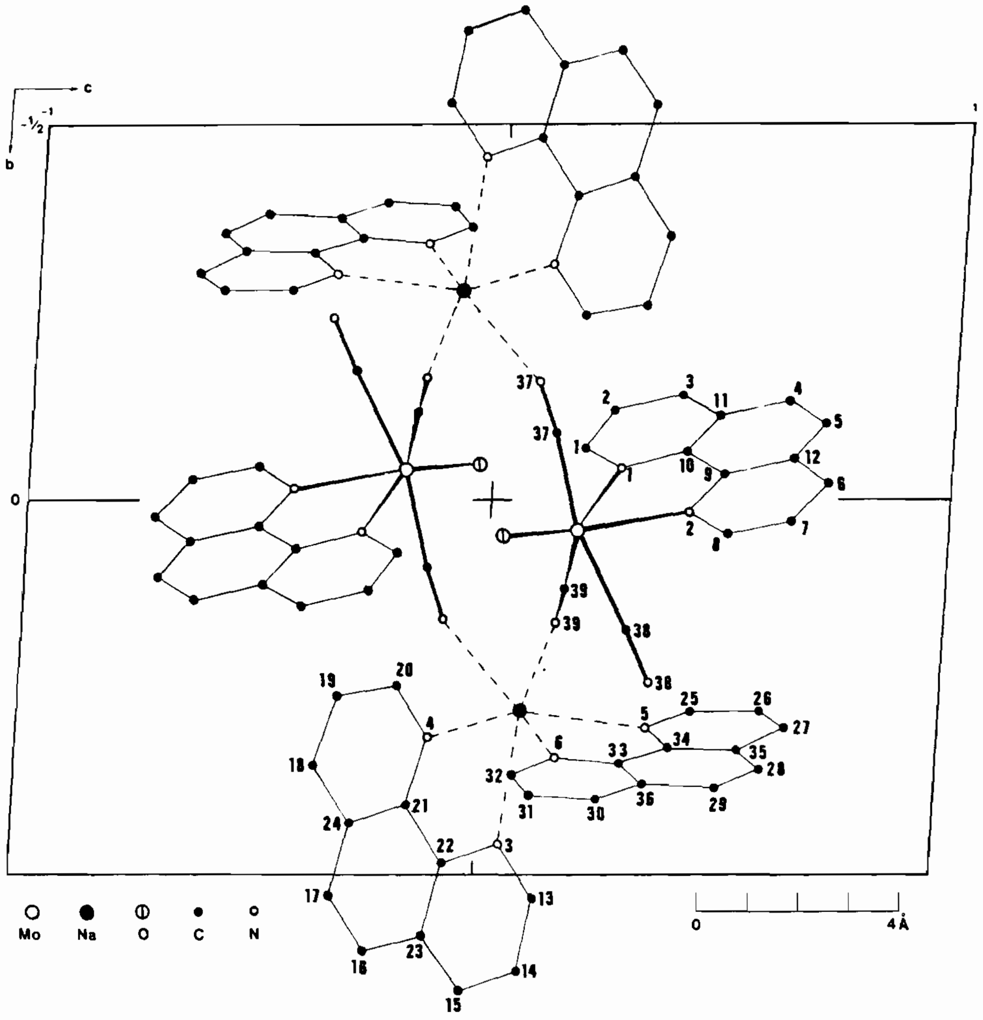


Fig. 1. Projection of the structure onto the (100) plane. Numbering of atoms according to Table I. Dashed lines: cation–anion and -phen interactions.

decomposition of the crystal was detectable during the data collection. A total of 4736 independent reflections were measured of which 3353 were considered as observed, $I \geqslant 3\sigma(I)$. Only Lorentz and polarization corrections were applied.

The co-ordinates of the molybdenum atom were determined from a three-dimensional Patterson function and those of the remaining non-hydrogen atoms from a subsequent Fourier map. A full-matrix least-squares refinement, using all the observed reflections and anisotropic temperature parameters for all the atoms, converged after 7 cycles at $R = 0.069$.

The atomic scattering factors (interpolated for Mo(IV)) were those tabulated by Cromer and Waber [8]. A list of the observed and calculated structure factors may be obtained from the authors. The final atomic co-ordinates and anisotropic thermal parameters are listed in Table I.

Results and Discussion

A projection of the structure along the *a* axis is presented in Fig. 1. One phen molecule is chelated to the molybdenum atom whilst the remaining two are attached to the sodium ion by ion-dipole interactions through the N atoms. The six-atom grouping around each sodium ion is completed by two additional cation-anion interactions consisting of the nitrogen end of a cyanide ligand of each of two symmetry related $[\mathrm{MoO(CN)_3(phen)}]^-$ ions. The nitrogen atoms of these cyanide ligands bond at an angle of 94.1(3)° at the sodium ion. Figure 1 also shows that the two *cis*-orientated cyanide ligands at an angle of C(37)–Mo–C(39) = 87.3(4)° represent the sole anionic contacts to surrounding symmetry related sodium ions. These almost rectlinear Mo–C≡N chains of approximate equal length

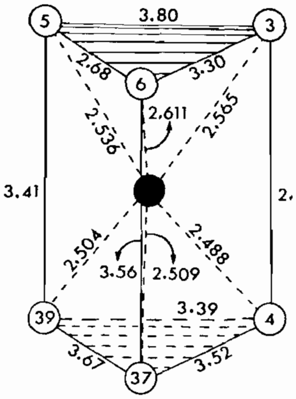


Fig. 2. Distances (Å) for the approximate trigonal prismatic environment of sodium ions. N atom numbering according to Table I. N(37) corresponds to the 1 – x, ȳ, z̄ transformed co-ordinate.

forming bond angles of C(37)–N(37)–Na′ = 159.9(8)° and C(39)–N(39)–Na = 165.9(9)° respectively, give rise to a rhombic-like arrangement consisting of alternating sodium and molybdenum atoms. The large phen molecules, being on the outskirts of this cation–anion arrangement, result in van der Waals forces being further the only stabilizing factor between this arrangement and similar ones in the crystal. The complex, in contrast to being a salt, thus behaves like a covalent compound for ex. being moderately soluble in polar solvents like methanol and acetone. It is also noticeable that hydrogen bonds, originating from the inclusion of crystal water in many alkali metal or acid cyano complexes [1, 9, 10] and which serve primarily as stabilizing cation to cyanide ligand interactions, are absent in the present case. The N(38) atom has as a result of this only a closest contact of 3.31 Å with a carbon atom of a neighbouring phen molecule.

The sodium ion has a distorted trigonal prismatic environment (Fig. 2). The N(3), N(5), N(6) and N(4), N(37), N(39) planes form an angle of 14.5° whilst the normals to the four-atom planes N(5)–N(6)–N(37)–N(39), N(3)–N(4)–N(37)–N(6) and N(3)–N(4)–N(39)–N(5) form angles of 115.0, 124.8 and 119.4° in the above cyclic order respectively. The bond distances in Fig. 2 show that the sodium ion is roughly in the centre of the prism which is also manifested in its distances from the above-mentioned four-atom planes ranging from 0.89 to 1.05 Å. The shortest edges of the trigonal prism in Fig. 2 *i.e.* N(3)–N(4) and N(5)–N(6), represent the bite distances of the phen molecules, which as can be seen, lead to considerable distortion.

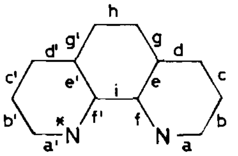
A helpful criterion for distinction between the octahedral $O_h(D_{3d})$ and trigonal prismatic D_{3h} forms is the dihedral angle (δ) or twist angle (ϕ), [11]. The theoretical values are: δ = 70.5° (D_{3d}) and 0, 90, 120° (D_{3h}); ϕ = 60° (D_{3d}) and 0° (D_{3h}). We calculated ϕ = 0° in excellent agreement with the theoretical value and implicating zero twist, relative to each other, for the three-atom planes in Fig. 2. The averaged δ-values for the three different sets were calculated as 15.7, 79.1 and 125.5° which strongly favour the chosen model but also illustrate the distortion along the edge lengths and diagonals of the four-atom planes in Fig. 2. The rigid N(3)–N(4) bite of 2.696(9) Å results in a contraction of this edge length relative to the N(5)–N(39) and N(6)–N(37) edges and is also responsible for the aforementioned inclination of the triangular planes.

The chemical equivalent bond distances and angles of the phen molecules are given in Table II. Averaged bond distances are also compared with Pauling's [12] π-bond orders derived for the similar phenanthrene molecule in terms of valence bond theory. The averaged bond distances in Table II agree well with the expected values except for types *a* and *f* which involve C–N bonds. The same phenomenon was encountered in the crystal structure of 1,10-phenanthroline [13] and the averaged values for a host of other phen complexes [14]. Both the *a* and *f* types are 0.04–0.06 Å shorter than Pauling's values which is not significant as the majority of these structure determinations have high standard deviations for these bonds. However, theoretical values calculated by a SCF-MO method [13] (a = 1.330, f = 1.347 Å) agree far better with those of the present and other structures. The averaged bond angles in Table II are in fair agreement with those of other structure determinations. Calculations showed the phen rings to be planar with a maximum deviation of 0.05 Å for any single atom from its specific plane.

An interesting feature of the phen molecule, being rigid and having a fairly constant intramolecular N···N distance (2.639(9), 2.696(9) and 2.682(13) Å for phen 1, 2 and 3 respectively), is the correlation between the metal–nitrogen bond distance and the N–M–N bite angle. An approximate linear correlation was found to be operative for bite angles between 75 and 85° and corresponding M–N distances between *ca.* 2.25 and 2.0 Å respectively [14]. Our structural results with N(1)–Mo–N(2) = 71.0(2), N(3)–Na–N(4) = 64.5(2) and N(5)–Na– N(6) = 62.8(3)° with corresponding averaged M–N distances of 2.268, 2.527 and 2.574 Å respectively, support the latter finding in that this correlation being valid and extendible to N–M–N angles as small as those for phen 2 and 3. Considering the different bond types between sodium and molybdenum atoms to phen molecules it is clear that the above-mentioned correlation is largely a function of effective metallic radii alone.

The Mo bonded atoms in the $[MoO(CN)_3(phen)]^-$ ion form a distorted octahedron. The N(1), C(38),

TABLE II. Bond Distances (Å) and Angles (°) within the 1,10-Phenanthroline Molecules (e.s.d. s in parentheses).



The asterisk implies the lower coded N atom of each phen ring. Phen 1 is bonded to Mo whilst phen 2 and 3 correspond to those rings containing the N(3) and N(5) atoms respectively.

Bond	Phen 1	Phen 2	Phen 3	Av[a]	π-order
a	1.314(11)	1.320(11)	1.310(20)	1.325(5)	0.6
a′	1.326(11)	1.328(11)	1.349(15)		
b	1.411(14)	1.424(15)	1.409(23)	1.411(6)	0.4
b′	1.403(14)	1.413(16)	1.405(17)		
c	1.389(14)	1.384(16)	1.348(23)	1.368(7)	0.6
c′	1.371(15)	1.357(17)	1.360(22)		
d	1.396(13)	1.415(12)	1.402(20)	1.404(6)	0.4
d′	1.404(12)	1.406(13)	1.399(20)		
e	1.415(12)	1.388(13)	1.397(14)	1.405(5)	0.4
e′	1.407(12)	1.419(13)	1.404(14)		
f	1.367(11)	1.357(12)	1.343(14)	1.352(7)	0.4
f′	1.366(11)	1.355(12)	1.325(12)		
g	1.424(13)	1.446(15)	1.431(19)	1.432(6)	0.2
g′	1.432(13)	1.423(15)	1.435(19)		
h	1.362(13)	1.346(13)	1.322(22)	1.343(8)	0.8
i	1.389(11)	1.439(11)	1.427(15)	1.418(7)	0.2

Angle	Phen 1	Phen 2	Phen 3	Av[a]
af	118.0(7)	118.0(8)	117.2(10)	118.0(3)
a′f′	118.5(7)	117.4(8)	118.7(9)	
ab	122.8(8)	122.8(10)	123.6(14)	122.7(4)
a′b′	121.6(9)	123.4(10)	122.1(11)	
bc	120.1(8)	118.2(8)	118.8(16)	119.5(4)
b′c′	120.8(8)	119.5(9)	119.6(13)	
cd	117.9(9)	119.9(10)	119.5(13)	118.8(4)
c′d′	118.5(9)	118.9(10)	118.0(12)	
de	118.3(8)	116.7(7)	117.1(11)	117.9(4)
d′e′	117.7(8)	117.9(9)	119.6(11)	
ef	122.9(7)	124.5(7)	123.7(10)	123.1(3)
e′f′	122.8(7)	122.8(7)	121.8(10)	
ei	121.4(8)	118.2(8)	118.3(10)	119.3(3)
e′i	118.5(8)	119.4(8)	120.0(9)	
eg	119.1(8)	121.8(8)	120.9(11)	120.3(3)
e′g′	120.6(8)	120.0(8)	119.1(11)	
gh	120.2(9)	119.3(10)	120.3(12)	120.4(4)
g′h	120.2(9)	121.2(10)	121.3(13)	

[a] E.s.d. s were estimated from $\sigma = [1/\Sigma_i(1/\sigma_i^2)]^{1/2}$ for i individual values.

C(39), C(37) equatorial plane is planar with a maximum deviation of 0.004 Å for any individual atom. This plane stems from the original one containing the four cyanide ligands in the parent $[MoO_2(CN)_4]^{4-}$ ion. Calculations also show that the Mo atom is displaced by a significant 0.33 Å out of the aforementioned plane towards the oxygen atom. This coupled with the fixed N(1)····N(2) bite distance and accompanying bite angle of 71.0(2)° (instead of the required 90°) gives considerable distortion as evidenced in the shape determining angles of Table III.

Ligand-ligand repulsion is an important determinative factor in the stereochemistry of six-coordinate complexes. The theoretical results for the minimization of repulsion energies [15] for the case of [M(bidentate)(unidentate)$_4$] complexes has practical stereochemical implications which can be applied to the $[MoO(CN)_3(phen)]^-$ ion. By defining the equatorial plane and ligands normal to it (Fig. 3),

TABLE III. Parameters of the Coordination Octahedron (e.s.d.'s in parentheses).

A. Bond and edge lengths (Å)

Type	Length	Type	Length	Type	Length
Mo–O	1.659(7)	C(38)–N(38)	1.16(1)	O–C(37)	2.91(1)
Mo–N(1)	2.174(7)	C(39)–N(39)	1.16(1)	O–C(38)	2.94(1)
Mo–N(2)	2.363(7)	N(1)–N(2)	2.639(9)	O–C(39)	2.96(1)
Mo–C(37)	2.161(10)	N(2)–C(37)	3.03(1)	N(1)–C(37)	3.08(1)
Mo–C(38)	2.179(10)	N(2)–C(38)	2.90(1)	N(1)–C(38)	3.07(1)
Mo–C(39)	2.092(9)	N(2)–C(39)	3.18(1)	C(37)–C(39)	2.94(1)
C(37)–N(37)	1.14(1)	O–N(1)	2.83(1)	C(38)–C(39)	2.93(1)

B. Selected angles (°)

Type	Angle	Type	Angle	Type	Angle
N(1)–Mo–N(2)	71.0(2)	N(1)–Mo–C(37)	90.6(3)	N(1)–C(38)–C(39)	89.0(4)
N(2)–Mo–C(38)	79.3(3)	C(37)–Mo–C(39)	87.3(4)	C(38)–C(39)–O(37)	93.9(4)
N(2)–Mo–C(37)	84.0(3)	C(38)–Mo–C(39)	86.7(4)	N(1)–C(37)–C(39)	88.8(4)
N(2)–Mo–C(39)	90.7(3)	N(1)–Mo–C(38)	89.9(3)	Mo–C(37)–N(37)	172.5(8)
O–Mo–N(1)	94.4(3)	N(1)–Mo–C(39)	161.7(3)	Mo–C(38)–N(38)	177.4(8)
O–Mo–C(37)	98.6(4)	C(37)–Mo–C(38)	162.2(3)	Mo–C(39)–N(39)	178.2(9)
O–Mo–C(38)	99.2(4)	O–Mo–N(2)	165.3(3)		
O–Mo–C(39)	103.8(4)	C(38)–N(1)–C(37)	88.3(3)		

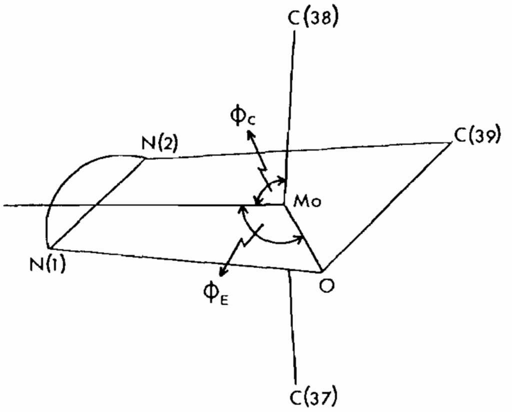


Fig. 3. Perspective view of molybdenum bonded atoms for comparison of repulsion energy parameters [15].

the *cis*-octahedron should possess mm symmetry for unidentate ligands of the same kind and the symmetrical bidentate one having the same donor atoms. In such a case it should have $\phi_C = 90°$, $\phi_E = 135°$ and a normalized bite (donor–donor atom distance in chelate divided by its metal–donor atom distance), b, of 1.41 for the ideal octahedron. The $[MoO(CN)_3(phen)]^-$ ion has only C_1 site symmetry and two kinds of unidentate ligands so that individual repulsions for the unidentate ligands rather than averaged values should be considered. We calculated b = 1.16, $\phi_C = 83.1°$ (for C(38)), 86.4° (for C(37)) and $\phi_E = 131.6°$ (for O) and 124.4° (for C(39)). For the latter b value (representative of a fixed ligand design for the present case) minimum repulsion energies should prevail at $\phi_C \approx 92°$ and $\phi_E \approx 131°$. The ϕ_C values for C(38) and C(37) and the ϕ_E value of C(39) deviate by more than 6° from the required respective values which is indicative of non-bonded repulsions operating on these three atoms.

TABLE IV. Selected van der Waals Distances (A) with e.s.d.'s in Parentheses.

Bond type	Distance	Bond type	Distance
C(38)···C(39)	2.93(1)	C(37)···C(39)	2.94(1)
C(38)···O	2.94(1)	C(37)···O	2.91(1)
C(38)···N(1)	3.07(1)	C(37)···N(1)	3.08(1)
C(38)···N(2)	2.90(1)	C(37)···N(2)	3.03(1)
O·······N(1)	2.83(1)	O·······C(39)	2.96(1)

Taking van der Waals radii of 1.6 Å for carbon in covalent cyanides [16], 1.5 and 1.4 Å for nitrogen and oxygen respectively [17], it is evident that the above-mentioned repulsions can be justified by the C(38)····C(39) and C(37)····C(39) distances in Table IV. Both are *ca.* 0.25 Å shorter than expected. It is also noticeable that only C(38)····N(2) deviate by *ca.* 0.2 Å whilst other C····N distances correlate well with the expected value. This is the expected result since the out-of-plane Mo atom, which is strongly bonded to oxygen and with this Mo=O bond normal to the equatorial N(1), C(37), C(39), C(38) plane, will force the latter four atoms closer together resulting in the repulsion interactions outlined above.

The bond distances in Table III show two interesting results: the Mo–N(2) bond *trans* to the Mo=O bond is significantly 0.189 Å longer than the Mo–N(1) bond and secondly, the significant shortening by 0.078 Å in the Mo–C(39) bond compared to the average of Mo–C(37) and Mo–C(38) bond distances.

The lengthening of the Mo–N(2) relative to the Mo–N(1) bond is a direct consequence of the large *trans* influence of the terminal oxo group as was found for several oxomolybdenum(V) and dioxomolybdenum(VI) compounds [18]. Comparable bond distances for Mo–N(2) = 2.363(7) Å and Mo–N(1) = 2.174(7) Å are: 2.137(8) Å (*trans* to N) in *trans*-dichlorobis(N-methylsalicylaldiminato)-molybdenum(IV) [19]. 2.210(6) Å (*trans* to Cl), 2.408(6) Å (*trans* to O) for $MoOCl(tox)_2$ and 2.374(9) as well as 2.382(9) Å (both *trans* to O) for $MoO_2(tox)_2$ where tox = 8-mercaptoquinolinate ligands [20].

The short Mo=O distance of 1.659(7) Å is similar to that of *cis-mer*-$[MoOCl_2(PMe_2Ph)_3]$ (1.676(7) Å) [21] and 1.668(5) Å in the $[MoO(OH_2)(CN)_4]^{2-}$ ion [2], all suggestive of considerable pπ–dπ bonding. These distances are significantly different from the Mo=O bond distance of 1.834(9) Å in the *trans*-$[MoO_2(CN)_4]^{4-}$ ion [1] and also apparently 0.03–0.04 Å shorter than the 1.698(7) Å distance in the $[MoO(OH)(CN)_4]^{3-}$ ion [2]. It was qualitatively concluded that the longer Mo=O bond in the $[MoO_2(CN)_4]^{4-}$ ion was the result of overconcentration of negative charge within the limited volume of this ion [1]. This argument seems to be true in comparing the Mo=O bond lengths of $[MoO_2(CN)_4]^{4-}$, $[MoO(OH)(CN)_4]^{3-}$, $[MoO(OH_2)(CN)_4]^{2-}$ and $[MoO(CN)_3(phen)]^-$ ions where a substantial shortening of 0.175 Å is observable for this series. The $[MoO(CN)_3(phen)]^-$ ion, as a result of the incompatibility of the phen ligand with regular octahedral geometry, shows greater distortion compared to the other Mo(IV) cyano complexes, with the result that ligand–ligand repulsions could be responsible for the observed bond lengths as well. In this respect it was for ex. found that the Mo=O bond length of 1.803(11) Å in $[MoOCl_2(PEt_2Ph)_3]$ was 0.127(13) Å longer than that of $[MoOCl_2(PMe_2Ph)_3]$ due to different steric requirements of the phosphine ligands [22].

The average dimensions of the Mo–C≡N chains in Table III agree well with those of the aforementioned oxocyano as well as octacyano complexes [23, 24] of Mo(IV). The exception is the significant 7.5° deviation from linearity for the Mo–C(37)–N(37) angle. This can be related to the strong Na′····N(37) interaction (see Fig. 1) and smaller Na′–N(37)–C(37) angle compared to the Na–N(39)–C(39) angle (*vide supra*). The significant shorter Mo–C(39) distance is possibly the result of preferred backbonding from the metal to the π* orbital of the cyanide ligand (twice as much as for the other two *trans*-orientated cyanide ligands [25]) utilizing the two metal d electrons from the nonbonding d_{xy} orbital [26]. This is the first authenticated case for π-bonding in tetra- or octacyano complexes of Mo(IV). The degree of π-bonding in these complexes is normally difficult to assess due to insignificant differences between individual Mo–C bond distances. The dodecahedral D_{2d} stereochemical form allows, as an example, π-bonding participation in the four B ligand sites only [24] which could be verified for the $Nb(CN)_8^{5-}$ ion [27] but not for $Mo(CN)_8^{4-}$, $Mo(CN)_8^{3-}$ and $Nb(CN)_8^{4-}$ ions in the course of structure determinations.

The operative mechanism for the preferred π-shortening of the Mo–C(39) bond in contrast to an expected less drastic but equal reduction of all three Mo–C bonds could possibly be explained in conjunction with the structural *trans* influence. The carbon donor atom of the cyanide ligand has a greater *trans* influence than the nitrogen donor atom of the phen ligand which would lead to an expected shortening of the Mo–C bond *trans* to the nitrogen atom in contrast to two *trans* disposed cyanide ligands with longer Mo–C bonds. A similar case was encountered in the bis(maleonitriledithiolato)-1,10-phenanthrolinecobaltate(III) ion where Co–S distances *trans* to nitrogen atoms were shortened by 0.034 Å [28].

This structure determination revealed a hitherto unknown substitution reaction of $[MoO_2(CN)_4]^{4-}$ ions, expressed by the equation $[MoO_2(CN)_4]^{4-} + L{-}L + 2H^+ \rightleftharpoons [MoO(CN)_3(L{-}L)]^- + H_2O$ where L–L = bidentate ligands. The acid dependence of this equilibrium implies the participation of one or more of the dioxo, oxohydroxo or oxoaquo forms during this reaction, which is the object of a kinetic study under way. The fact that a cyanide ligand can be displaced by use of bidentate chelates offers a vast field of substitution chemistry to be exploited.

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